STUDY OF THE ADHESIVE BONDING OF A THERMOPLASTIC COMPOSITE MATERIAL BASED ON POLYPROPYLENE AND GLASS FIBER

C. Palleiro[a*], E. Rodríguez-Senín[a], R. Losada[a], R. de la Mano[a]

[a] *AIMEN Technology Center, Advanced Materials, C/Relva 27A – 36410 – Porriño – Spain*

**clara.palleiro@aimen.es*

Keywords: thermoplastic composite, adhesive bonding, surface treatment, atmospheric plasma

Abstract

In this paper, the results obtained in the set-up of the adhesive bonding process applied to polypropylene reinforced with glass fiber (PP-GF) are presented. This article is concerned with the influence of surface treatment on the strength of single lap joints. An epoxy adhesive and different surface treatments were tested: abrasive (sanding), chemical (sulfo-chromic disolution) and energetic (atmospheric plasma). The results obtained by mechanical and chemical characterization are compared with those obtained by welding techniques (ultrasonic, induction and resistance welding).

1. Introduction

Polymer matrix composites (PMCs) are materials that consist of a polymer matrix into which polymer fibers are incorporated. The great advantages of using these materials lie in combining the good properties of the polymers such as oxidation resistance, light weight, thermal and electrical insulation and ductility, with high mechanical resistance and the stiffness of the fibers which are added. Generally, PMCs are classified according to the nature of the polymer matrix, so thermoplastic matrix composites (TPC) and thermosetting matrix composites (TSC) can be found. Although nowadays TSCs monopolize two thirds of the current market of polymer matrix composites, the TPC are increasingly replacing them since thermoplastic resins with great mechanical and chemical properties have been developed. The increased interest in the TPC is due, among other reasons, to the better fatigue performance and impact, as well as its manufacturing processes in which there is no volatile emission and does not require autoclave curing process. It is estimated that the global market for TPC will reach 6.2 billion dollars in 2014 [1] [2].

One of the major drawbacks of TPCs is that available geometries of these materials are relatively simple (2D or simple profiles), so it is necessary to carry out the union of these components to develop 3D structures. Traditionally these connections are made by mechanical elements, as in TSCs. However, this technology shows a number of drawbacks such as stress concentrations created by the presence of holes and cutouts, also in these cases appear delamination problems due to localized wear which occurs during drilling operations, problems of differential thermal expansion between fasteners the material of a plastic nature, water entering between fixing elements and possible galvanic corrosion problems in the joints, also additional weight increase due to the restraint system. Due to these disadvantages,

the main goal is to replace mechanical elements for other type of joints which do not have these drawbacks. In this sense adhesive and welded joints offer great potential.
Adhesives are used to bond different components in many applications, where structures are subject to stress loads in services. The main advantage of adhesive bonding is that the stress is distributed over the whole bonded area, so the stress concentrations are minimized. In adhesive bonding, the surface characteristics of the materials to be joined play a key role, as well, surface treatments have a huge transcendence in joint quality [3]. The objective of any surface treatment is to modify the chemistry or morphology of a thin layer of the material surface that promotes the adhesive bond without affecting the characteristics and properties of the substrate. The effectiveness of the surface treatment will depend on such factors as the nature of the material and the intensity of treatment.
Adhesive bonding of thermoplastic composite material (polypropylene reinforced with glass fiber, PP-GF) has been analyzed in this paper. There are very few studies on the adhesive bonding of these materials, and therefore more suitable surface treatments are not dealt. Some recommended methods for conventional (non reinforced thermoplastics and thermosetting composites) were chosen in this study. The aim is to analyze and optimize the adhesive bond on a thermoplastic composite.

2. Materials and experimental procedure

The thermoplastic composite sheets used in this work were provided by ACCIONA. The laminates are formed by four woven balanced bidirectional layers of E-glass fibers/ polypropylene matrix , of a thickness between 2.7 and 3.2 mm, with a “wave twill 2/2” fabric reinforcing. The total fiber fraction was 62,7%.
The bonding study was performed by shear strength single lap joint tests, so the surface treatments were applied on the lap region of rectangular specimens of 100 mm x 25 mm dimensions (Figure 1) following UNE-EN 1465:1996 [4].

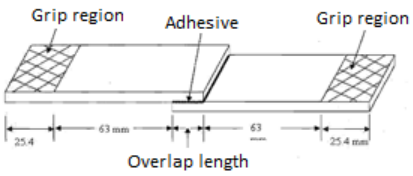

Figure 1. Specimen configuration for mechanical tests

2.*1. Surface preparation and characterization*

Polypropylene is a nonpolar polymer that has maximum value of 40 mJ/m [5] of surface energy what means that the adhesion properties are very low. The treatments considered to improve the shear strength of the adhesive lap joints in this study are summarized below:

Sanding (Physical Treatment) - main effect of this treatment is physical modification of the surface, creating a roughened area and increasing the surface area which improves the adhesive-substrate interaction by mechanical anchorage. During this type of treatment potential surface chemical contaminants are also eliminated. This treatment was carried out with a 200 grit sandpaper, in the way as no fibers become exposed, so the last layer of polymer should not be fully removed. Sanding will modify morphology of the surface, and remove contamination at the same time [6].

Sulfuric acid-dichromate solution (Chemical Treatment) – treatment suggested by ASTM D2093 [7] This is not a specific standard for thermoplastic composites but it is generally applicable for surface activation of plastics. The treatment consists of immersing the

specimens in a sulfochromic bath for 1 hour, with subsequent washing and drying in an oven at 37ºC for 1 hour. Chemical treatment was used to alter chemically the surface of the polymer creating polar groups

Atmospheric plasma (Energetic Treatment) - PlasmaBeam Standard equipment of Diener Electronic has been employed, installed on an ABB robot. A routine covering the whole overlap of the specimen is programmed, so the plasma treatment is applied automatically, with air as the process gas, ensuring speed (10 mm/s) and plasma nozzle-substrate distance (15 mm) uniformity. Only one pass was made with the plasma treatment, in order to oxidize the surface of the specimens, because of the influence of the excited atoms, ions and free radicals contained in the flame.

The effect of surface treatments used was defined by three surface characterization techniques. First, the surface energy of the test pieces was measured after the application of treatment using calibrated surface tension inks (Figure 2). Subsequently, the samples were analyzed by Fourier Transform Infrared spectroscopy using a JASCO 600 equipment, with a Germanium ATR device. In order to measure the surface roughness after treatment, a profilometer Veeco Dektak 8M was used in this study. Test conditions were established following the standard UNE-EN-ISO 4288, using a 25 µm tip radio, and an applied force of 15 mg, in a measuring range 1 mm for 40 seconds [8].

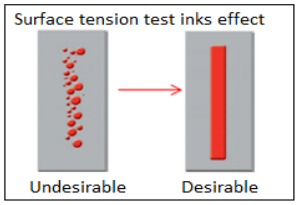

Figure 2. Surface tension measurement of a material with an ink set

2.2 *Adhesive bonding*

ARALDITE 2014-1 (Huntsman) structural bicomponent epoxy adhesive, characterized by its high load capacity, was used. The specimen assembly was made by placing some gauges (0,10 µm) to achieve the optimum adhesive thickness according to technical sheets. Figure 3 shows the assembly sequence of the specimens.

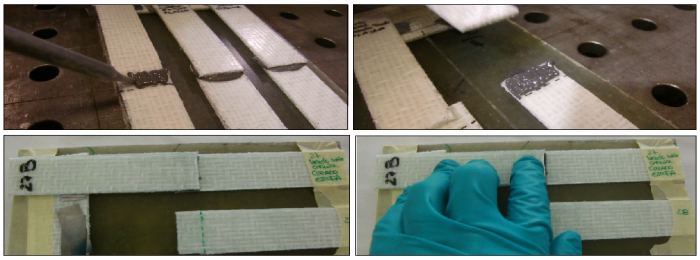

Figure 3. Assembly sequence of the adhesive joints

Another factor to consider in order to obtain a perfect bonding is the curing process. In this case, epoxy adhesive curing was made by two methods: at room temperature and curing in an oven (Lento WF120) at 60ºC for 20 minutes. The curing time and temperature of this last method were selected according to the specifications of the adhesive, in order to obtain the higher strength of the joint.

2.3 Shear tensile tests

The shear tensile tests were performed using an electromechanical Universal machine from HOYTOM, according to the recommendation of UNE EN 1465:1996 Standard [9]. Five specimens were tested for each condition, at room temperature and with a displacement rate of 1.3 mm/min. The tensile shear strength value is determined from the equation given by:

$$\tau = \frac{Fmax}{L \times b} \left[\frac{N}{mm^2}\right] \quad (1)$$

Where τ is the shear strength (N/mm^2), overlap length L (mm), b overlap width (mm) and Fmax maximum tensile force applied (N).

3. Experimental results and discussion

3.1 Surface Characterization

Tests on the base material for this study were carried out, and the surface energy values obtained were around 28 mN/m. This is not enough for the adhesive substrate interaction leads to a good bond, and requires the application of surface treatment procedures, in order to increase its surface energy [10]. After applying different surface treatments (sanding, chemical, plasma), an improvement of the surface energy value can be seen, reaching all of them values of surface energy between 38 and 44 mN/m. This is a clear increase compared to the base material without any treatment.

Parallel to surface energy measurements, FTIR analysis were carried out to check the effect of surface treatments at a chemical level on the surface of the material. Figure 4 shows the four spectra of the surface with the three different surface treatments and the untreated sample.

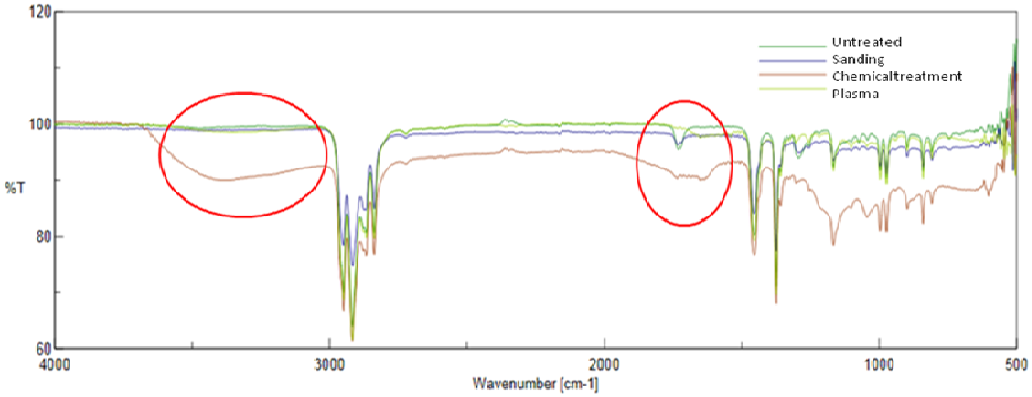

Figure 4. FTIR spectra of PP+GF treated and untreated specimens

Only the bands associated with polypropylene appear for both untreated sample and sanded sample, such as CH_2/CH_3 vibration bands between 2800-2900 cm^{-1}, bands associated with symmetric and asymmetric CH_3 bending between 1300-1480 cm^{-1}, and bands associated with the vibration of C-C bonds between 800-1200 cm^{-1}. Regarding the samples subjected to plasma treatment and chemical treatment, new bands are observed, associated with carbonyl and carboxyl groups between 1500-1700 cm^{-1} and hydroxyl groups (3300 cm^{-1}) conforming the creation of polar functional groups by the action of energetic and chemical treatments [11]. Such changes are perceived in a more intense way by the action of chemical treatment than with plasma treated specimens.

Roughness values are shown in Table 1. The effect of sanding treatment has the biggest effect in the roughness, while the chemical has not a significant effect. In the case of atmospheric

plasma, high dispersed values have been obtained. As it can be seen in the graphics obtained (Figure 5), sanding treatment of the samples resulted in a homogeneous high rough surface. Atmospheric plasma treatment obtained some high roughness values, but not uniformly at the treated area. Referring to chemical treatment, a small change is observed in the surface roughness. Those surface unevennesses can also be detected on the untreated sample, so it is concluded that this effect appears because of the fiber weave. In areas where weft thread passes over one or more warp threads, surface discontinuities can be observed.

Table 1. Roughness average measurements

Sample	Roughness measurements (Ra, µm)	
	Longitudinal measurement	**Transverse dimension**
Untreated samples	0,68	0,44
Sanding	1,70	1,63
Chemical Treatment	0,87	0,65
Atmospheric plasma	1,25	Dispersed values

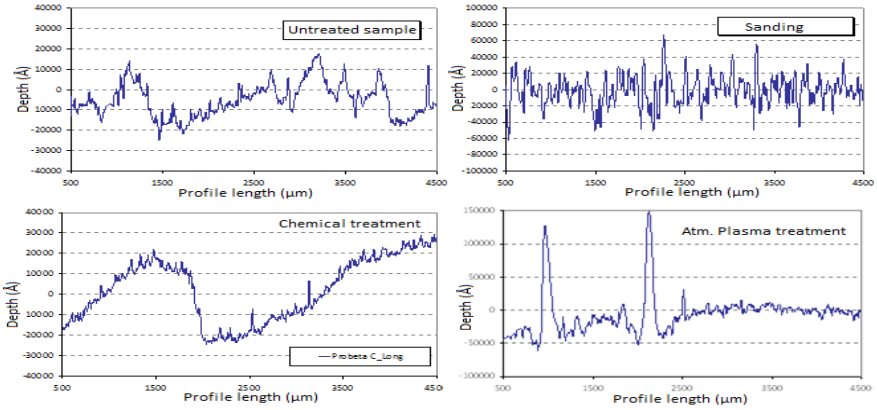

Figure 5. Roughness results obtained by profilometry

3.2 Mechanical Characterization of the Adhesive Bonds

The results of the mechanical characterization tests of the adhesive joints, in terms of maximum resistance and failure type, carried out with the different combinations of surface treatment, adhesive and curing process, are shown at Table 2 below. All the joints, where a surface treatment was applied, achieved higher strength compared with untreated specimen. Furthermore, the oven curing has also a positive effect in the strength.

Table 2: Adhesive bonding conditions and tensile shear test results

Surface treatment	Curing process	Ultimate tension strength (MPa)	Failure type
No treated	Room temperature	0,82 ± 0,09	Adhesive failure
	Oven (60ºC, 20 min)	0,75 ± 0,15	Adhesive failure
Sanding	Room temperature	2,97 ± 0,33	Mixed failure
	Oven (60ºC, 20 min)	3,28 ± 0,27	Mixed failure
Chemical treatment	Room temperature	2,76 ± 0,71	Mixed failure
	Oven (60ºC, 20 min)	4,47 ± 0,58	Mixed failure
Atmospheric plasma	Room temperature	2,79 ± 0,36	Adhesive-Mixed
	Oven (60ºC, 20 min)	2,49 ± 0,38	Adhesive-Mixed

When the type of failure in the bonded area is analyzed, three different failure modes can be distinguished: adhesive, cohesive and mixed failure. Adhesive failure is produced when the bond is weak, and the fracture is produced at the interface between the adhesive and the adherent, because the bond is weaker than the own adhesive. Cohesive failure is produced when the bond is as strong as the own adhesive, so fracture occurs within the adhesive. This failure mechanism is desirable as is normally related to high values of resistance. The mixed type of failure occurs when the failure mechanism varies between adhesive and cohesive within the entire area of overlap. In this work, the predominant failure mode was the adhesive fracture, and in sanding and chemical treated specimens, simultaneous separation of the polypropylene and the glass fiber at the surface adjacent to the adhesive also occurred (Figure 6).

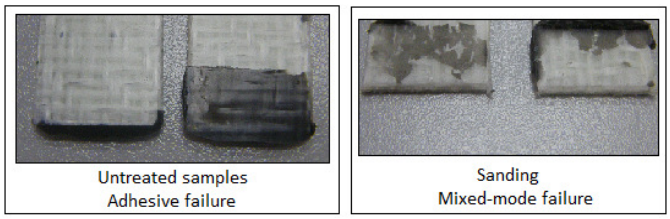

Figure 6. Failure type of epoxy adhesive bonds

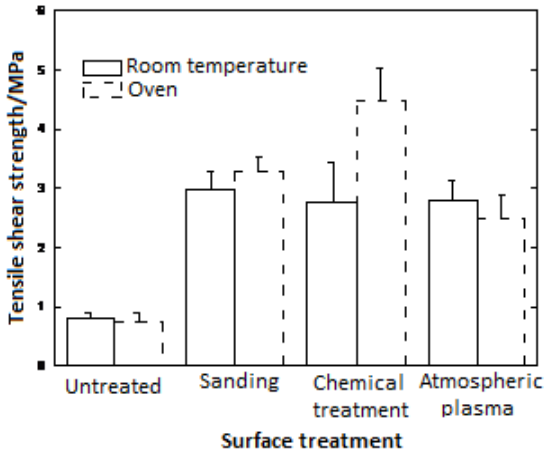

Figure 7: Results obtained at tensile shear tests according to the different surface treatment

In view of the results presented in Table 2 and Figure 7, it is found that when using the epoxy adhesive and curing takes place at room temperature, samples have not undergone any treatment have a very low shear strength, around 0.82 MPa, and failure mode presented is purely adhesive, which certifies the poor quality of the joint. On the other hand, at these same conditions, all specimens subjected to surface treatments exhibit much higher strength values compared to untreated material, about 70% higher. The differences seen in terms of shear strength values achieved with various surface treatments are below 7%. From which it follows that under these conditions all treatments have a similar efficiency for the enhancement of the union.

When the adhesive is cured in an oven, untreated specimens plasma and sanding treatment showed no significant differences in terms of strength values obtained under these conditions and at room temperature. However, in the case of chemically treated samples, strength values with the oven curing, are 40% higher than those achieved with curing at room temperature and nearly 90% higher than obtained for untreated samples. Therefore, when curing is performed at room temperature, all the treatments experimented a similar improvement compared to the untreated samples, but when the curing is effected in an oven significant differences appear to yield by far the best results with the samples subjected to chemical

treatment. Interestingly, the resistance values obtained in the atmospheric plasma treated samples have not demonstrated the expected results, since in all the tests performed so far the resistance values obtained are of the same order or even lower than the results obtained with abrasive treatment (sanding). It is known that atmospheric plasma treatments are not as effective for polymers such as polypropylene or PTFE as chemical treatments [12], however one would expect, based on the bibliographic results [13] to achieve shear strength values greater than those observed with the abrasive treatment. In this sense it is necessary to continue working on the optimization of this process in order to get higher bond strength.

Welding vs Adhesive Bonding

Since the adhesive bonding technology for these thermoplastic materials compete with welding, the results obtained by both processes are compared. Lap shear strength values obtained with welded joints are between two and three times higher than that obtained in adhesive joints (Table 3).

Table 3: Lap shear strength values of welded joints [14]

Welding technique	Ultimate strength (MPa)
INDUCTION welding	8,23 ± 1,97
ULTRASOUNDS welding	9,95 ± 1,20
RESISTANCE welding	13,35 ± 1,25
ADHESIVE bonding (epoxy)	2,50 – 4,50

The current lines of work aim to reduce the differences between the adhesive bonding and welding techniques through the optimization of surface treatment methods. Although the welded joints in all cases provide higher strength values, the difficulty in many cases of application must be taken into account. One of the greatest advantages of the adhesives is that most of the connections can be made in situ, while the welding techniques will be limited by the equipment required and the need in many cases to employ filler metal materials to carry them out. Against these drawbacks, adhesive bonds are still convenient, despite their lower strength.

4. Conclusions

This work presents the effectiveness of three surface treatments, including atmospheric plasma, sanding and chemical procedure, resulting in all of them an important increase of the shear tensile strength compared with untreated sample. Room temperature curing shows similar strength values but when 60ºC curing is applied, an important increase occurs in the chemical treatment.

The results obtained by surface plasma treatment were not as good as expected. Since this was a first experience with this type of materials, the goal of future studies will be the optimization of treatment with atmospheric plasma to further improving the adhesive bond. Furthermore, a research by using adhesives with different properties (flexible adhesives, for example) will also be carried out in the future.

References

[1] *Opportunities in Global Thermoplastic Composites 2009-2014: Trends, Forecast, and Opportunity Analysis*, Market Publishers, Report Database

[2] Pereira da Costa A, Cocchieri Botelho E, Leali Costa M, Eiji Narita N, Tarpani JR *A review of welding technologies for thermoplastic composites in aerospace applications.* JATM (2012)
[3] *Surfaces, chemistry & applications.* Edited by M. Chaudhury and A.V. Pocius. ELSEVIER (Adhesion science and engineering-2), 2002
[4] UNE EN 1465:1996. *Adhesivos. Determinación de la resistencia a la cizalladura por tracción de juntas pegadas de substratos rígidos*.
[5] *Adhesive Bonding. Science, technology and applications*. Edited by R. D. Adams, Woodhead Publishing Ltd, 80-88, 279-304.
[6] P.N.B Reis, J.M. Ferreira, M.O.W Richardson *Effect of the surface preparation on PP reinforced glass fiber adhesive lap joint strength,* Journal of Thermoplastic Composite Materials 2012 25:3.
[7] ASTM D2093-03. *Standard Practice for Preparation of Surfaces of Plastics Prior to Adhesive Bonding*
[8] UNE-EN ISO 4288:1998. *Especificación geométrica de producto (GPS). Calidad superficial: Método del perfil. Reglas y procedimientos para la evaluación del estado superficial*.
[9] UNE EN 1465:1996. Adhesivos. Determinación de la resistencia a la cizalladura por tracción de juntas pegadas de substratos rígidos.
[10] D. M. Brewis *Adhesion to polyethylene and polypropylene* School of Chemistry, Leicester Polytechnic, Leicester LE1 9BH, UK, and D. Briggs ICI Plastics Division, Welwyn Garden City, Hertfordshire AL 7 1HD, UK (Received 13 August 1 980)
[11] *The Use of the Spectrometric Technique FTIR-ATR to Examine the Polymers Surface* Wieslawa Urbaniak-Domagala, Technical University of Lodz, Department of Material and Commodity Sciences and Textile Metrology, Poland
[12] Jeandrau JP. *Investigation into the effect of surface treatment on the wettability and the bondability of low surface energy materials.* Adhesive joints, 121-136, 1984.
[13] Encinas N, Abenojar JM Martinez MA. *Development of improved polypropylenen adhesive bonding by abrasion and atmospheric plasma surface modification.* International Journal of Adhesion and Adhesives 33, 1-6, 2012
[14] Losada R, de la Mano R, Palleiro C, Rodriguez E. *"An induction welding study of glass fibre reinforced polypropylene composite"*17th International Conference on Composite Structures (ICCS17), Porto, 17-20 June 2013